Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1208). Services for accessing these data are described at the back of the journal.

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2-*O*-Benzoyl-*myo*-inositol-1,3,5-orthoformate†

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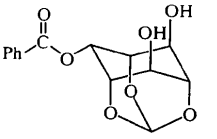
Abstract

Protected *myo*-inositol derivatives are important precursors in the synthesis of phosphorylated *myo*-inositol derivatives, which play a significant role in cellular signal transduction. The structure of the title compound, $C_{14}H_{14}O_7$, which was prepared from *myo*-inositol, has been determined by X-ray crystallography. Several types of hydrogen-bonding interactions are involved in the packing of the molecule in the crystal.

Comment

myo-Inositol and its phosphorylated derivatives play an important role in the cellular signalling process (Potter & Lampe, 1995) and have been the subject of theoretical studies (Liang *et al.*, 1994). *myo*-Inositol-1,3,5-orthoformate and its derivatives are important intermediates for the synthesis of several *myo*-inositol phosphates (Das & Shashidhar, 1997, and references therein). The title compound, (I), is a key intermediate for the synthesis of *myo*-inositol pentaphosphates (Ozaki *et al.*, 1994; Chung & Chang, 1996). We present here the crystal structure of (I), which was prepared in a one-pot procedure from *myo*-inositol.



(I)

The structure of (I) (Fig. 1) resembles that of *myo*-inositol-1,3,5-orthoformate (Uhlmann & Vasella, 1992). The O1—C1, O3—C3 and O5—C5 bonds are longer than the corresponding lengths from the respective O atoms to C7 by 0.03, 0.05 and 0.05 Å, respectively (Table 1). There are a few potential hydrogen-bond interactions, of both the O—H···O and C—H···O types (Table 2). The crystal density (1.513 Mg m^{-3}) is relatively high, indicating a tight packing of molecules in the lattice. The hydroxyl group at O6 is involved in three-centre hydrogen bonding (Taylor *et al.*, 1984; Jeffrey & Maluszynska, 1982) with two acceptor O atoms, one intra- and the other intermolecular, resulting in a large deviation from linearity of the *D*—H···*A* angles. The O6 atom also acts as the acceptor for two more C—H···O interactions.

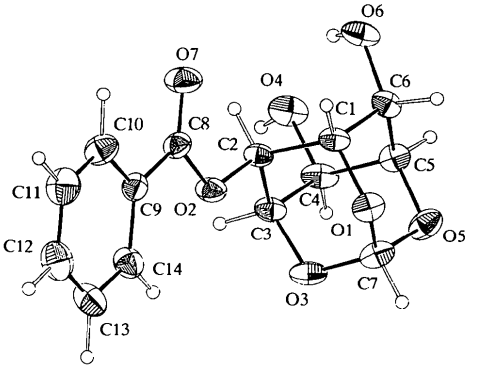


Fig. 1. *ZORTEP* (Zsolnai, 1995) diagram of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

myo-Inositol (2.7 g, 0.015 mol), trimethylorthoformate (2.39 g, 0.0225 mol), *p*-toluenesulfonic acid monohydrate (0.25 g, 1.31 mmol) and dry DMF (20 ml) were mixed and heated at

† Alternative name: 2-*O*-benzoyl-1:3:5-tri-*O*-methylidyne-*myo*-inositol.

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373 K with stirring for 3 h. The clean solution was cooled to room temperature, then triethylamine (1 ml) was added to the mixture and low-boiling liquids were evaporated *in vacuo*. Dry benzene was added and again evaporated *in vacuo* (2 × 5 ml). The residue was cooled to 273 K, and pyridine (10 ml) and benzoyl chloride (2.2015 g, 0.015 mol) were added dropwise over a period of 30 min. The reaction mixture was warmed to room temperature and stirred for 8 h. Then the reaction mixture was concentrated *in vacuo* and the gummy residue obtained chromatographed over silica gel (60–120 mesh, 100 g) using 15% ethyl acetate/petroleum ether as eluent to obtain the title compound (2.5 g, 57%). For the crystallographic investigation, the compound was recrystallized from chloroform (m.p. 482 K).

Crystal data

$C_{14}H_{14}O_7$
M_r = 294.25
Monoclinic
$P2_1/n$
a = 6.184 (2) Å
b = 17.787 (4) Å
c = 11.746 (2) Å
β = 91.65 (2)°
V = 1291.5 (6) Å^3
Z = 4
D_x = 1.513 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14.84–22.72°
μ = 0.123 mm^{-1}
T = 293 (2) K
Prism
0.70 × 0.55 × 0.40 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2284 measured reflections
2284 independent reflections
1846 reflections with $I > 2\sigma(I)$

θ_{max} = 25°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.222
S = 1.082
2284 reflections
190 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1710P)^2 + 0.2638P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.460 e Å^{-3}
$\Delta\rho_{min}$ = −0.469 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.406 (3)	O6—C6	1.410 (3)
O1—C1	1.444 (3)	O7—C8	1.199 (3)
O2—C8	1.350 (3)	C1—C2	1.517 (3)
O2—C2	1.440 (3)	C1—C6	1.530 (3)
O3—C7	1.388 (4)	C2—C3	1.518 (3)
O3—C3	1.442 (3)	C3—C4	1.526 (4)
O4—C4	1.412 (3)	C4—C5	1.523 (4)
O5—C7	1.398 (3)	C5—C6	1.521 (4)
O5—C5	1.448 (3)	C8—C9	1.478 (4)
C7—O1—C1	111.1 (2)	C5—C4—C3	107.6 (2)
C8—O2—C2	116.2 (2)	O5—C5—C6	107.4 (2)
C7—O3—C3	110.9 (2)	O5—C5—C4	107.8 (2)
C7—O5—C5	110.8 (2)	C6—C5—C4	112.0 (2)
O1—C1—C2	108.8 (2)	O6—C6—C5	114.4 (2)
O1—C1—C6	107.4 (2)	O6—C6—C1	111.7 (2)
C2—C1—C6	111.0 (2)	C5—C6—C1	107.0 (2)
O2—C2—C1	110.4 (2)	O3—C7—O5	112.4 (2)
O2—C2—C3	107.0 (2)	O3—C7—O1	111.1 (2)
C1—C2—C3	107.5 (2)	O5—C7—O1	110.4 (2)
O3—C3—C2	109.5 (2)	O7—C8—O2	123.0 (2)
O3—C3—C4	107.7 (2)	O7—C8—C9	125.4 (2)
C2—C3—C4	110.0 (2)	O2—C8—C9	111.6 (2)
O4—C4—C5	108.4 (2)	C10—C9—C8	119.0 (2)
O4—C4—C3	111.3 (2)	C14—C9—C8	122.4 (2)
C7—O1—C1—C2	59.4 (3)	O4—C4—C5—C6	60.6 (3)
C7—O1—C1—C6	−60.9 (3)	C3—C4—C5—C6	−59.9 (3)
C8—O2—C2—C1	80.6 (3)	O5—C5—C6—O6	176.4 (2)
C8—O2—C2—C3	−162.7 (2)	C4—C5—C6—O6	−65.4 (3)
O1—C1—C2—O2	60.7 (2)	O5—C5—C6—C1	−59.3 (2)
C6—C1—C2—O2	178.7 (2)	C4—C5—C6—C1	58.9 (3)
O1—C1—C2—C3	−55.7 (2)	O1—C1—C6—O6	−175.1 (2)
C6—C1—C2—C3	62.3 (3)	C2—C1—C6—O6	66.1 (3)
C7—O3—C3—C2	−59.5 (3)	O1—C1—C6—C5	58.9 (2)
C7—O3—C3—C4	60.0 (2)	C2—C1—C6—C5	−59.9 (3)
O2—C2—C3—O3	−62.8 (2)	C3—O3—C7—O5	−62.1 (3)
C1—C2—C3—O3	55.8 (2)	C3—O3—C7—O1	62.2 (2)
O2—C2—C3—C4	179.1 (2)	C5—O5—C7—O3	61.6 (3)
C1—C2—C3—C4	−62.3 (3)	C5—O5—C7—O1	−63.1 (3)
O3—C3—C4—O4	−177.1 (2)	C1—O1—C7—O3	−62.5 (3)
C2—C3—C4—O4	−57.9 (3)	C1—O1—C7—O5	62.9 (3)
O3—C3—C4—C5	−58.4 (3)	C2—O2—C8—O7	3.1 (4)
C2—C3—C4—C5	60.8 (3)	C2—O2—C8—C9	−175.4 (2)
C7—O5—C5—C6	61.8 (3)	O7—C8—C9—C10	−3.4 (4)
C7—O5—C5—C4	−59.1 (3)	O2—C8—C9—C10	175.2 (2)
O4—C4—C5—O5	178.5 (2)	O7—C8—C9—C14	178.2 (3)
C3—C4—C5—O5	58.0 (2)	O2—C8—C9—C14	−3.3 (3)

Table 2. *Hydrogen-bonding geometry and other close interactions (Å, °)*

For the C—H···O interactions, C···O distances < 3.5 Å, H···O < 2.6 Å and C—H···O angles > 110° have been considered.

D—H···A	H···A	D···A	D—H···A
C3—H3···O7^{i}	2.534	3.463 (3)	150.2
C4—H4···O6^{i}	2.413	3.370 (3)	159.6
C13—H13···O5^{ii}	2.588	3.314 (4)	127.1
C14—H14···O6^{iii}	2.515	3.350 (3)	138.8
O4—HO4···O1^{iv}	1.881	2.732 (2)	150.0
O6—HO6···O3^{v}	2.383	3.058 (3)	123.9
O6—HO6···O4	1.909	2.711 (3)	134.8

Symmetry codes: (i) $1 + x, y, z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$; (v) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

The title structure was solved by direct methods using *MULTAN*80 (Main *et al.*, 1980). H atoms, located from difference Fourier maps, were used in the structure-factor calculations, but were not refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (PC Version; Gabe *et al.*, 1989). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93 and Microsoft Word 6.0.

Dr T. Linden kindly provided us with the coordinates of a *myo*-inositol structure. US and TP are grateful to the Council of Scientific and Industrial Research, New Delhi, India, for fellowships. This work was supported by the Department of Science and Technology, New Delhi, India.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1052). Services for accessing these data are described at the back of the journal.

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3-(*N*-Benzyl-*N*-methylcarbamoyl)-1,2,4-trimethylquinolinium Iodide

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Abstract

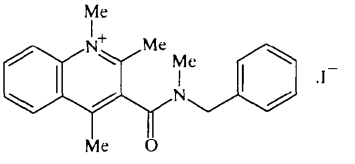
The title compound, $C_{21}H_{23}N_2O^+.I^-$, possesses a central planar carbamoyl fragment in which the carbonyl and *N*-methyl groups are in *anti* positions. Located perpendicular to this central fragment on opposite sides are the *N*-benzyl group and the quinolinium fragment. This conformation leads to an axial chirality. The compound crystallizes as a racemate in a centrosymmetric space group.

Comment

In previous investigations, it has been shown that the rotation of an aromatic ring system about the connecting bond to a carbamoyl group is sterically hindered if there are two methyl groups in *ortho* positions. The ring is therefore stabilized in a conformation perpendicular to the carbamoyl group (Smeets *et al.*, 1988).

The benzyl group is a popular N-protecting group in organic chemistry. A total of 118 compounds bearing a benzyl–N(*R*)–C(O)*R* fragment can be found in the Cambridge Structural Database (October 1997 release; Allen & Kennard, 1993). A statistical analysis shows a nearly Gaussian distribution of the torsion angles of the N—C_{benzyl} bond about the maxima at 90 and −90°. Semi-empirical *MNDO* [Dewar & Thiel (1977); as implemented in *MOPAC*6.0 (Stewart, 1990)] calculations also suggest energy minima at torsion angles of 90 and −90°, with a rotational barrier of 3.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}).

We report here the results of our analysis of the title compound, (I). A view of the molecule with the numbering scheme is shown in Fig. 1. We find a nearly perpendicular situation on both sides of the carbamoyl



(I)

group of the title compound involving the *N*-benzyl and quinolinium fragments [torsion angles C2—C1—C13—O 79.9 (3) and C13—N2—C15—C16 88.1 (3)°] resulting in an axial chirality. In contrast to similar compounds (van Hooff *et al.*, 1982; Bastiaansen *et al.*, 1986, 1988), the title compound does not undergo spontaneous enantiomeric resolution, but crystallizes as a racemate in the centrosymmetric space group $P2_1/c$. In accordance with these older investigations, the carbonyl and *N*-methyl groups are in *anti* positions in the carbamoyl group.

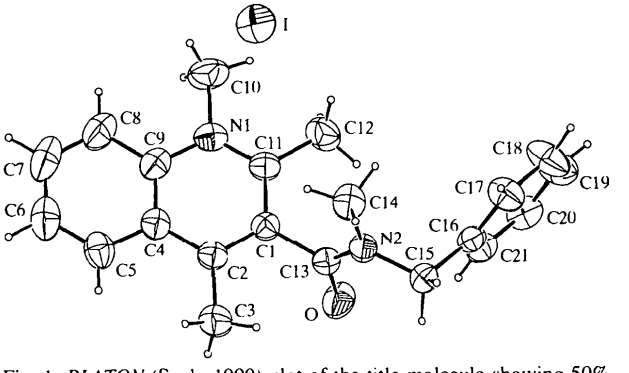


Fig. 1. *PLATON* (Spek, 1990) plot of the title molecule showing 50% probability displacement ellipsoids.